

(19)



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(11)

EP 0 920 461 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:

17.10.2001 Bulletin 2001/42

(21) Application number: **98930782.2**

(22) Date of filing: **02.06.1998**

(51) Int Cl.7: **C08F 10/00, C08F 4/642**

(86) International application number:
PCT/EP98/03289

(87) International publication number:
WO 98/56834 (17.12.1998 Gazette 1998/50)

(54) COMPONENTS AND CATALYSTS FOR THE POLYMERIZATION OF OLEFINS

KATALYSATOR-KOMPONENTE UND KATALYSATOREN FÜR DIE POLYMERISATION VON
OLEFINEN

COMPOSANTS ET CATALYSEURS POUR LA POLYMERISATION D'OLEFINES

(84) Designated Contracting States:
AT BE DE ES FI FR GB GR IT NL SE

(30) Priority: **09.06.1997 IT MI971349**

(43) Date of publication of application:
09.06.1999 Bulletin 1999/23

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(56) References cited:
EP-A- 0 086 644 EP-A- 0 125 911
EP-A- 0 360 491 JP-A- 8 157 521

• **LOCATELLI P: "ZIEGLER-NATTA CATALYSTS:
NO END IN SIGHT TO INNOVATION" TRENDS IN
POLYMER SCIENCE, vol. 4, no. 10, October 1996,
pages 326-329, XP000625975**

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EP 0 920 461 B1

Description

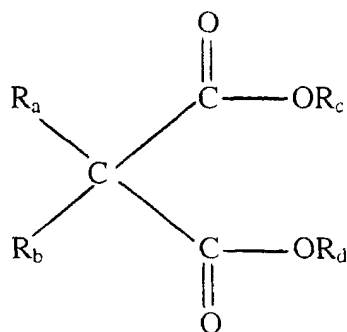
[0001] The present invention relates to catalyst components for the polymerization of olefins, to the catalyst obtained therefrom and to the use of said catalysts in the polymerization of olefins $\text{CH}_2=\text{CHR}$ in which R is hydrogen or a hydrocarbyl radical with 1-12 carbon atoms. In particular the present invention relates to catalyst components, suitable for the stereospecific polymerization of olefins, comprising a titanium compound having at least a Ti-halogen bond and an electron donor compound selected from esters of malonic acid having a particular formula supported on a Mg halide. Said catalyst components used in the polymerization of olefins, and in particular of propylene, are capable to give polymers in high yields and with high isotactic index expressed in terms of high xylene insolubility.

[0002] The use of some esters of malonic acid as internal electron donors in catalysts for the polymerization of propylene is already known in the art.

[0003] In EP-A-45977 is disclosed the use of an ester of the malonic acid (diethyl diisobutylmalonate) as internal donor of a catalyst for the polymerization of olefins. EP-A-86473 discloses a catalyst for the polymerization of olefins comprising (a) an alkyl compound, (b) an electron donor compound having certain reactivity features towards MgCl_2 and (c) a solid catalyst component comprising, supported on MgCl_2 , a Ti halide and an electron donor selected from many classes of ester compounds including malonates. In particular, the use of diethyl allylmalonate and di-n-butyl malonate as internal donors in a catalyst for the polymerization of propylene is exemplified. From EP-A-86644 is known the use of diethyl n-butyl malonate and diethyl isopropylmalonate as internal donors in Mg-supported catalysts for the polymerization of propylene in which the external donor is a heterocyclic compound or a ketone. The European patent EP-B-125911 discloses a process for producing (co)polymers which comprises (co)polymerizing at least one olefin, optionally with a diolefin, in the presence of a catalyst composed of (a) a solid catalyst component containing Mg, Ti and an electron donor compound selected from esters of polycarboxylic acids, (b) an organometallic compound of a metal selected from group I to III of the periodic table, and (c) an organosilicon compound having a Si-O-C or a Si-N-C bond. Examples of preferred esters compounds include diethyl methylmalonate, diethyl butylmalonate, diethyl phenylmalonate, diethyl diethylmalonate, and diethyl dibutylmalonate. Only the use of a catalyst containing diethyl phenylmalonate has been exemplified in the preparation of polypropylene.

[0004] However, a common drawback experienced in the use of the above mentioned malonates was represented by a poor polymerization yield and/or a not suitable isotactic index of the final polymer.

[0005] JP-08157521 relates to a process for preparing a solid catalyst component for polymerization of olefins which is characterized by contacting a solid catalyst component produced by the reaction among a magnesium compound, a titanium compound and an halogen compound, with one or more of electron donating compounds represented by the general formula:

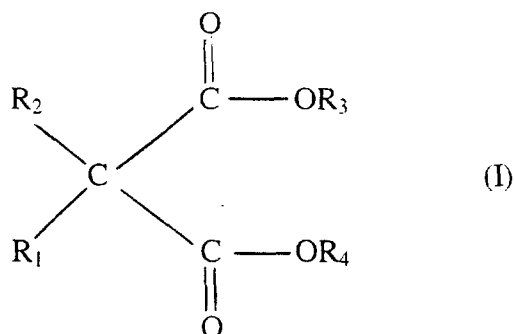


wherein R_c and R_d are, independently selected from the group consisting of: a straight-chain or branched hydrocarbon group having 1-10 carbon atoms, and R_a and R_b are independently selected from an aliphatic or cyclic saturated hydrocarbon group containing one or more secondary or tertiary carbons and having 3-20 carbon atoms. According to this patent the fact that the substituents R_a and R_b are branched is very important.

[0006] It has now surprisingly been found that another class of malonate esters wherein one substituent in 2 position is selected from a linear alkyl, alkenyl, aryl, arylalkyl or alkylaryl group, when used as an internal electron donor, leads to higher polymerization yields compared to those obtainable by using the electron donors of the prior art still maintaining very high stereoselectivity. This is particularly surprising in view of the direct teaching of JP-A-08157521, which excluded this class of compounds.

[0007] It is therefore an object of the present invention a solid catalyst component for the polymerization of olefins $\text{CH}_2=\text{CHR}$ in which R is hydrogen or a hydrocarbyl radical with 1-12 carbon atoms, comprising a titanium compound, having at least a Ti-halogen bond, and an electron donor compound supported on a Mg halide, in which said electron

donor is selected from esters of malonic acids of formula (I):



wherein R_1 is a C_1 - C_{20} linear or branched alkyl, C_3 - C_{20} alkenyl, C_3 - C_{20} cycloalkyl, C_6 - C_{20} aryl, arylalkyl or alkylaryl group; R_2 is a C_1 - C_{20} linear alkyl, C_3 - C_{20} linear alkenyl, C_6 - C_{20} aryl, arylalkyl or alkylaryl group; R_3 and R_4 are independently selected from the group consisting of C_1 - C_3 alkyl, cyclopropyl, with the proviso that when R_1 is C_1 - C_4 linear or branched alkyl or alkenyl, R_2 is different from R_1 ; preferably R_2 is primary linear C_1 - C_{20} alkyl or a primary C_6 - C_{20} arylalkyl group.

[0008] These new electron donors permit to obtain higher yields in the polymerization process with respect to the catalyst containing the malonates known in the art.

[0009] Specific examples of preferred disubstituted malonates compounds are:

diethyl-2,2-dibenzylmalonate, dimethyl-2-n-butyl-2-isobutylmalonate,
 diethyl-2-n-butyl-2-isobutylmalonate, diethyl-2-isopropyl-2-n-butylmalonate,
 diethyl-2-methyl-2-isopropylmalonate, diethyl-2-methyl-2-isobutylmalonate,
 diethyl-2-isobutyl-2-benzylmalonate.

[0010] The magnesium halide is preferably MgCl_2 in active form which is widely known from the patent literature as a support for Ziegler-Natta catalysts. Patents USP 4,298,718 and USP 4,495,338 were the first to describe the use of these compounds in Ziegler-Natta catalysis. It is known from these patents that the magnesium dihalides in active form used as support or co-support in components of catalysts for the polymerization of olefins are characterized by X-ray spectra in which the most intense diffraction line that appears in the spectrum of the non-active halide is diminished in intensity and is replaced by a halo whose maximum intensity is displaced towards lower angles relative to that of the more intense line.

[0011] The preferred titanium compounds used in the catalyst component of the present invention are TiCl_4 and TiCl_3 ; furthermore, also Ti-haloalcoholates of formula $\text{Ti}(\text{OR})_n\text{X}_y$, where n is the valence of titanium and y is a number between 1 and n , can be used.

[0012] The preparation of the solid catalyst component can be carried out according to several methods.

[0013] According to one of these methods, the magnesium dichloride in an anhydrous state, the titanium compound and the electron donor compound of formula (I) are milled together under conditions in which activation of the magnesium dichloride occurs. The so obtained product can be treated one or more times with an excess of TiCl_4 at a temperature between 80 and 135°C. This treatment is followed by washings with hydrocarbon solvents until chloride ions disappeared.

[0014] According to a further method, the product obtained by co-milling the magnesium dichloride in an anhydrous state, the titanium compound and the electron donor compound of formula (I) is treated with halogenated hydrocarbons such as 1,2-dichloroethane, chlorobenzene, dichloromethane etc. The treatment is carried out for a time between 1 and 4 hours and at temperature of from 40°C to the boiling point of the halogenated hydrocarbon. The product obtained is then generally washed with inert hydrocarbon solvents such as hexane.

[0015] According to another method, magnesium dichloride is preactivated according to well known methods and then treated with an excess of TiCl_4 at a temperature of about 80 to 135°C which contains, in solution, an electron donor compound of formula (I). The treatment with TiCl_4 is repeated and the solid is washed with hexane in order to eliminate any non-reacted TiCl_4 .

[0016] A further method comprises the reaction between magnesium alcoholates or chloroalcoholates (in particular chloroalcoholates prepared according to U.S. 4,220,554) and an excess of TiCl_4 containing the electron donor compound (I) in solution at a temperature of about 80 to 120°C.

[0017] According to a preferred method, the solid catalyst component can be prepared by reacting a titanium compound of formula $Ti(OR)_{n-y}X_y$, where n is the valence of titanium and y is a number between 1 and n , preferably $TiCl_4$, with a magnesium dichloride obtained by dealcoholation of an adduct of formula $MgCl_2 \cdot pROH$, where p is a number between 0,1 and 6 and R is a hydrocarbon radical having 1-18 carbon atoms. The adduct can be suitably prepared in spherical form by mixing alcohol and magnesium chloride in the presence of an inert hydrocarbon immiscible with the adduct, operating under stirring conditions at the melting temperature of the adduct (100-130°C). Then, the emulsion is quickly quenched thereby causing the solidification of the adduct in form of spherical particles. Examples of spherical adducts prepared according to this procedure are described in USP 4,399,054. The so obtained adduct can be directly reacted with the Ti compound or it can be previously subjected to thermal controlled dealcoholation (80-130°C) so as to obtain an adduct in which the number of moles of alcohol is generally lower than 2.5 preferably between 0,1 and 1,5. The reaction with the Ti compound can be carried out by suspending the adduct (dealcoholated or as such) in cold $TiCl_4$ (generally 0°C); the mixture is heated up to 80-130°C and kept at this temperature for 0,5-2 hours. The treatment with $TiCl_4$ can be carried out one or more times. The electron donor compound of formula (I) can be added during the treatment with $TiCl_4$. The treatment with the electron donor compound can be repeated one or more times.

[0018] The preparation of catalyst components in spherical form are described for example in EP-A-395083, EP-A-553805, EP-A-553806.

[0019] The solid catalyst components obtained according to the above method show a surface area (by B.E.T. method) generally between 20 and 500 m^2/g and preferably between 50 and 400 m^2/g , and a total porosity (by B.E.T. method) higher than 0,2 cm^3/g preferably between 0,2 and 0,6 cm^3/g .

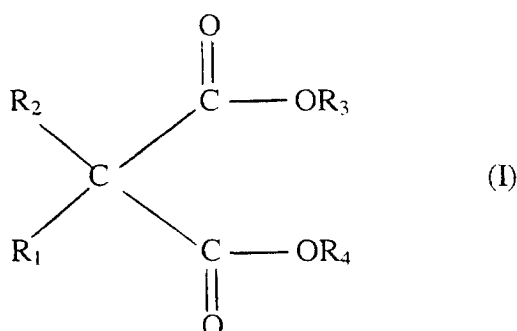
[0020] A further method to prepare the solid catalyst component of the invention comprises halogenating magnesium dihydrocarbyloxy compounds, such as magnesium dialkoxide or diaryloxy, with solution of $TiCl_4$ in aromatic hydrocarbon (such as toluene, xylene etc.) at temperatures between 80 and 130°C. The treatment with the $TiCl_4$ in aromatic hydrocarbon solution can be repeated one or more times, and the electron donor compound of formula (I) is added during one or more of these treatments.

[0021] In any of these preparation methods the desired electron donor compound of formula (I) can be added as such or, in an alternative way, it can be obtained *in situ* by using an appropriate precursor capable to be transformed in the desired electron donor compound by means, for example, of known chemical reactions such as esterification, transesterification etc. Generally, the electron donor compound of formula (I) is used in molar ratio with respect to the $MgCl_2$ of from 0,1 to 1 preferably from 0,05 to 0,5.

[0022] The solid catalyst component according to the present invention are converted to the catalysts for the polymerization of olefins by reacting them with organoaluminium compounds according to known methods.

[0023] In particular, it is an object of the present invention a catalyst for the polymerization of olefins $CH_2=CHR$, in which R is hydrogen or a hydrocarbyl radical with 1-12 carbon atoms, comprising the product of the reaction between:

- (i) a solid catalyst component comprising a titanium compound having at least a Ti-halogen bond, and an electron donor compound supported on a Mg halide in active form, in which said electron donor compound is selected from esters of malonic acids of formula (I):



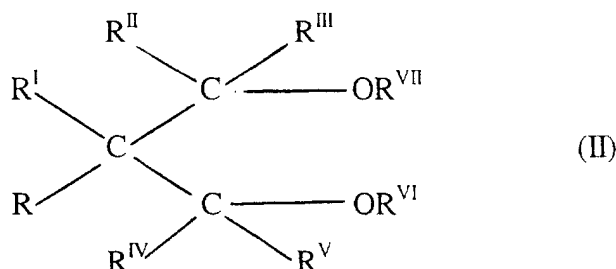
wherein R_1 is a C_1 - C_{20} linear or branched alkyl, C_3 - C_{20} alkenyl, C_3 - C_{20} cycloalkyl, C_6 - C_{20} aryl, arylalkyl or alkylaryl group; R_2 is a C_1 - C_{20} linear alkyl, C_3 - C_{20} linear alkenyl, C_6 - C_{20} aryl, arylalkyl or alkylaryl group; R_3 and R_4 are independently selected from the group consisting of C_1 - C_3 alkyl, cyclopropyl, with the proviso that when R_1 is C_1 - C_4 linear or branched alkyl or alkenyl, R_2 is different from R_1 ; preferably R_2 is primary linear C_1 - C_{20} alkyl or a primary C_6 - C_{20} arylalkyl group.

(ii) an alkylaluminium compound and,

(iii) one or more electron-donor compounds (external donor).

[0024] The alkylaluminium compound (ii) is preferably chosen among the trialkyl aluminium compounds such as for example triethylaluminium, triisobutylaluminium, tri-n-butylaluminium, tri-n-hexylaluminium, tri-n-octylaluminium. It is also possible to use mixtures of trialkylaluminium's with alkylaluminium halides, alkylaluminium hydrides or alkylaluminium sesquichlorides such as AlEt_2Cl and $\text{Al}_2\text{Et}_3\text{Cl}_3$.

[0025] The external donor (iii) can be of the same type or it can be different from the internal donor of formula (I). Suitable external electron-donor compounds include the ethers, the esters, the amines, heterocyclic compounds and particularly 2,2,6,6-tetramethyl piperidine, the ketones and the 1,3-diethers of the general formula (II):



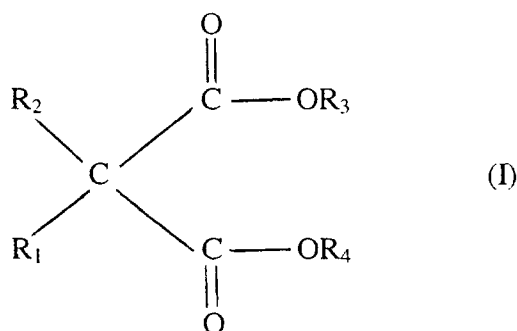
wherein R and R^I, R^{II}, R^{III}, R^{IV} and R^V equal or different to each other, hydrogen or hydrocarbon radicals having from 1 to 18 carbon atoms, and R^{VI} and R^{VII}, equal or different from each other, have the same meaning of R-R^I except that they cannot be hydrogen; one or more of the R-R^{VII} groups can be linked to form a cycle.

Particularly preferred are the external donors chosen among silicon compounds of formula $\text{Ra}^5\text{Rb}^6\text{Si}(\text{OR}^7)_c$, where a and b are integer from 0 to 2, c is an integer from 1 to 4 and the sum (a+b+c) is 4; R⁵, R⁶ and R⁷ are alkyl, cycloalkyl or aryl radicals with 1-18 carbon atoms. Particularly preferred are silicon compounds in which a is 1, b is 1 and c is 2. Among the compounds of this preferred class, particularly preferred are the compounds in which R₅ and/or R₆ are branched alkyl, cycloalkyl or aryl groups with 3-10 carbon atoms and R₇ is a C₁-C₁₀ alkyl group, in particular methyl. Examples of such preferred silicon compounds are methylcyclohexyldimethoxysilane, diphenyldimethoxysilane, methyl-t-butyldimethoxysilane, dicyclopentyldimethoxysilane. Moreover, are also preferred the silicon compounds in which a is 0, c is 3 and R⁶ is a branched alkyl or cycloalkyl group and R⁷ is methyl. Examples of such preferred silicon compounds are cyclohexyltrimethoxysilane, t-butyldimethoxysilane and hexyltrimethoxysilane.

[0026] The electron donor compound (iii) is used such an amount to give a molar ratio between the organoaluminium compound and said electron donor compound (iii) of from 0,1 to 500 preferably from 1 to 300 and more preferably from 3 to 100. As previously indicated, when used in the (co)polymerization of olefins, and in particular of propylene, the catalysts of the invention allow to obtain, with high yields, polymers having a high isotactic index (expressed by high xylene insolubility X.I.), thus showing an excellent balance of properties. This is particularly surprising in view of the fact that, as it can be seen from the comparison examples herebelow reported, the use as internal electron donors of malonate compounds known in the art gives poor results in term of yields and/or xylene insolubility thereby showing a very insufficient balance of properties.

[0027] Therefore, it constitutes a further object of the present invention a process for the (co)polymerization of olefins $\text{CH}_2=\text{CHR}$, in which R is hydrogen or a hydrocarbonyl radical with 1-12 carbon atoms, carried out in the presence of a catalyst comprising the product of the reaction between:

- (i) a solid catalyst component comprising a titanium compound having at least a Ti-halogen bond, and an electron donor compound supported on a Mg halide in active form, in which said electron donor compound is selected from esters of malonic acids of formula (I):



wherein R_1 is a C_1 - C_{20} linear or branched alkyl, C_3 - C_{20} alkenyl, C_3 - C_{20} cycloalkyl, C_6 - C_{20} aryl, arylalkyl or alkylaryl group; R_2 is a C_1 - C_{20} linear alkyl, C_3 - C_{20} linear alkenyl, C_6 - C_{20} aryl, arylalkyl or alkylaryl group; R_3 and R_4 are independently selected from the group consisting of C_1 - C_3 alkyl, cyclopropyl, with the proviso that when R_1 is C_1 - C_4 linear or branched alkyl or alkenyl, R_2 is different from R_1 ; preferably R_2 is primary linear C_1 - C_{20} alkyl or a primary C_6 - C_{20} arylalkyl group.

(ii) an alkylaluminium compound and,

(iii) one or more electron-donor compounds (external donor).

[0028] Said polymerization process can be carried out according to known techniques for example slurry polymerization using as diluent an inert hydrocarbon solvent, or bulk polymerization using the liquid monomer (for example propylene) as a reaction medium. Moreover, it is possible carrying out the polymerization process in gas-phase operating in one or more fluidized or mechanically agitated bed reactors.

[0029] The polymerization is generally carried out at temperature of from 20 to 120°C, preferably of from 40 to 80°C. When the polymerization is carried out in gas-phase the operating pressure is generally between 0,5 and 10 MPa, preferably between 1 and 5 MPa. In the bulk polymerization the operating pressure is generally between 1 and 6 MPa preferably between 1,5 and 4 MPa. Hydrogen or other compounds capable to act as chain transfer agents can be used to control the molecular weight of polymer.

[0030] The following examples are given in order to better illustrate the invention without limiting it.

CHARACTERIZATIONS

[0031] The diethyl malonates of formula (I) used in the present invention can be prepared according to known chemical synthesis as those described for example by J. March in "Advanced Organic Chemistry" IV Ed. (1992) pp. 464-468.

[0032] The malonates having R_3 and R_4 different from ethyl can be prepared by transesterification of the correspondent diethyl malonate as described in Example 1 of DE 2822472.

Propylene general polymerization procedure

[0033] In a 4 litre autoclave, purged with nitrogen flow at 70°C for one hour, 80 ml of anhydrous hexane containing 10 mg of solid catalyst component, 7 mmoles of AlEt_3 and 0.35 mmoles of dicyclopentylmethoxysilane were introduced in propylene flow at 30°C. The autoclave was closed, 3 NL of hydrogen were added and then, under stirring, 1.2 Kg of liquid propylene were fed. The temperature was raised to 70°C in five minutes and the polymerization was carried out at this temperature for two hours. The unreacted propylene was removed, the polymer was recovered and dried at 70°C under vacuum for three hours, and then it was weighed and fractionated with o-xylene to determine the amount of the xylene insoluble (X.I.) fraction at 25°C.

Determination of X.I.

[0034] 2.5 g of polymer were dissolved in 250 ml of o-xylene under stirring at 135°C for 30 minutes, then the solution was cooled to 25°C and after 30 minutes the insoluble polymer was filtered. The resulting solution was evaporated in nitrogen flow and the residue was dried and weighed to determine the percentage of soluble polymer and then, by difference, the X.I. %.

EXAMPLESExamples 1-8

Preparation of Solid Catalyst Components

[0035] Into a 500 ml four-necked round flask, purged with nitrogen, 225 ml of TiCl_4 were introduced at 0°C . While stirring, 10.3 g of microspheroidal $\text{MgCl}_2 \times 2.1\text{C}_2\text{H}_5\text{OH}$ (obtained by partial thermal dealcoholation of an adduct prepared as described in ex. 2 of USP 4,399,054 but operating at 3,000 rpm instead of 10,000) were added. The flask was heated to 40°C and 9 mmoles of malonate were thereupon added. The temperature was raised to 100°C and maintained for two hours, then the stirring was discontinued, the solid product was allowed to settle and the supernatant liquid was siphoned off.

[0036] 200 ml of fresh TiCl_4 were added, the mixture was reacted at 120°C for one hour and then the supernatant liquid was siphoned off. The solid was washed six times with anhydrous hexane (6 x 100 ml) at 60°C and then dried under vacuum: the malonates used, the amount of Ti (wt%) and of malonates (wt%) contained in the solid catalyst component are reported in table 1. The polymerization results are reported in table 2.

Comparative Examples 9, 10

Preparation of Solid Catalyst Component

[0037] The catalyst components have been prepared according to the same procedure of the examples 1-8 except for the fact that malonates different from those of formula (I) have been used. The malonates used, the amount of Ti (wt%) and of malonates (wt%) contained in the solid catalyst component are reported in table 1. The polymerization results are reported in table 2. As it can be seen from the above, the use of the electron donor compounds of formula (I) permit to obtain higher yields in the polymerization process with respect to the catalyst containing the malonates known in the art. In particular it is very surprising the fact that by changing for example from diethyl 2,2-diisobutyl malonate (comp. Ex. 9) to diethyl-2-n-butyl-2-isobutyl malonate (Ex. 6) the yield in the polymerization process increases from 20.1 to 39.5 KgPP/gCat.

Table 1

Solid catalyst component preparation		Solid catalyst component composition		
Ex. n.	Malonate type	Ti wt%	Malonate	
			type	wt%
1	diethyl 2-methyl-2-isopropyl	3.2	diethyl 2-methyl-2-isopropyl	10.9
2	diethyl 2-methyl-2-isobutyl	4.1	diethyl 2-methyl-2-isobutyl	9.7
3	diethyl 2-ethyl-2-sec-butyl	4.6	diethyl 2-ethyl-2-sec-butyl	12.9
4	diethyl 2-isopropyl-2-n-butyl	4.0	diethyl 2-isopropyl-2-n-butyl	14.5
5	dimethyl 2-n-butyl-2-isobutyl	3.8	dimethyl 2-n-butyl-2-isobutyl	16.3
6	diethyl 2-n-butyl-2-isobutyl	4.6	diethyl 2-n-butyl-2-isobutyl	15.1
7	diethyl 2-isobutyl-2-benzyl	4.9	diethyl 2-isobutyl-2-benzyl	14.5
8	diethyl 2,2-dibenzyl	4.7	diethyl 2,2-dibenzyl	14.1
comp.9	diethyl 2,2-diisobutyl	4.5	diethyl 2,2-diisobutyl	13.5
comp.10	diethyl 2,2-diallyl	3.9	diethyl 2,2-diallyl	8.6

Table 2

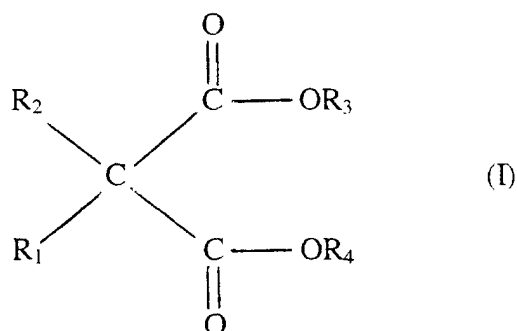
Example	Yield KgPP/gCat	X.I. %
1	35.5	96.8
2	35.8	96.6

Table 2 (continued)

Example	Yield KgPP/gCat	X.I. %
3	38.6	96.8
4	35.8	96.5
5	35.3	96.7
6	39.5	97.0
7	39.0	96.0
8	45.2	96.4
comp.9	20.1	96.7
comp.10	17.7	93.9

Claims

1. A solid catalyst component for the polymerization of olefins $\text{CH}_2=\text{CHR}$ in which R is hydrogen or a hydrocarbonyl radical with 1-12 carbon atoms, comprising a titanium compound, having at least a Ti-halogen bond and an electron donor compound supported on a Mg halide, in which said electron donor compound is selected from esters of malonic acids of formula (I):



wherein R_1 is a $\text{C}_1\text{-C}_{20}$ linear or branched alkyl, $\text{C}_3\text{-C}_{20}$ alkenyl, $\text{C}_3\text{-C}_{20}$ cycloalkyl, $\text{C}_6\text{-C}_{20}$ aryl, arylalkyl or alkylaryl group; R_2 is a $\text{C}_1\text{-C}_{20}$ linear alkyl, $\text{C}_3\text{-C}_{20}$ linear alkenyl, $\text{C}_6\text{-C}_{20}$ aryl, arylalkyl or alkylaryl group; R_3 and R_4 are independently selected from the group consisting of $\text{C}_1\text{-C}_3$ alkyl, cyclopropyl, with the proviso that when R_1 is $\text{C}_1\text{-C}_4$ linear or branched alkyl or alkenyl, R_2 is different from R_1 .

2. A solid catalyst component according to claim 1 in which R_2 is a $\text{C}_1\text{-C}_{20}$ linear alkyl, linear alkenyl, cycloalkyl, aryl, arylalkyl or alkylaryl group and R_1 is $\text{C}_1\text{-C}_4$ alkyl different from R_2 .
3. A solid catalyst component according to claim 1 in which at least R_1 or R_2 is primary $\text{C}_6\text{-C}_{20}$ arylalkyl group.
4. A solid catalyst component according to claim 1 in which the electron donor compound of formula (I) is selected from the group consisting of: diethyl 2,2-dibenzylmalonate, dimethyl-2-n-butyl-2-isobutylmalonate, diethyl-n-butyl-2-isobutylmalonate, diethyl-2-isopropyl-2-n-butylmalonate, diethyl-2-methyl-2-isopropylmalonate, diethyl-2-methyl-2-isobutylmalonate, diethyl 2-isobutyl-2-benzylmalonate.
5. A solid catalyst component according to claim 1 in which the magnesium halide is MgCl_2 in active form.
6. A solid catalyst component according to claim 1 in which the titanium compound is TiCl_4 or TiCl_3 .
7. A solid catalyst component according to claim 1 having a spherical form, a surface area between 20 and $500 \text{ m}^2/\text{g}$.

g, and a porosity higher than 0,2 cm³/g.

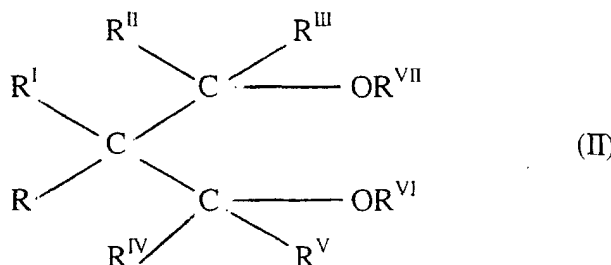
8. A catalyst for the polymerization of olefins CH₂=CHR, in which R is hydrogen or a hydrocarbyl radical with 1-12 carbon atoms, comprising the product of the reaction between:

- (i) the solid catalyst component of claim 1;
- (ii) an alkylaluminium compound and,
- (iii) one or more electron-donor compounds (external donor).

9. Catalyst according to claim 8 in which the alkylaluminium compound (ii) is a trialkyl aluminium compound.

10. Catalyst according to claim 9 in which the trialkyl aluminium compound is selected from the group consisting of triethylaluminium, triisobutylaluminium, tri-n-butylaluminium, tri-n-hexylaluminium, tri-n-octylaluminium.

11. Catalyst according to claim 8 in which the external donor (iii) is selected from the 1,3-diethers of the general formula (II):



wherein R and R^I, R^{II}, R^{III}, R^{IV} and R^V equal or different to each other, hydrogen or hydrocarbon radicals having from 1 to 18 carbon atoms, and R^{VI} and R^{VII}, equal or different from each other, have the same meaning of R-R^I except that they cannot be hydrogen; one or more of the R-R^{VII} groups can be linked to form a cycle.

12. Catalyst according to claim 8 in which the external donor (iii) is a silicon compound of formula. Ra⁵Rb⁶Si(OR⁷)_c, where a and b are integer from 0 to 2, c is an integer from 1 to 4 and the sum (a+b+c) is 4; R⁵, R⁶ and R⁷ are alkyl, cycloalkyl or aryl radicals with 1-18 carbon atoms

13. Catalyst according to claim 12 in which a is 1, b is 1 and c is 2.

14. Catalyst according to claim 13 in which R₅ and/or R₆ are branched alkyl, cycloalkyl or aryl groups with 3-10 carbon atoms and R₇ is a C₁-C₁₀ alkyl group, in particular methyl.

15. Catalyst according to claim 12 in which a is 0, c is 3 and R⁶ is a branched alkyl or cycloalkyl group and R⁷ is methyl.

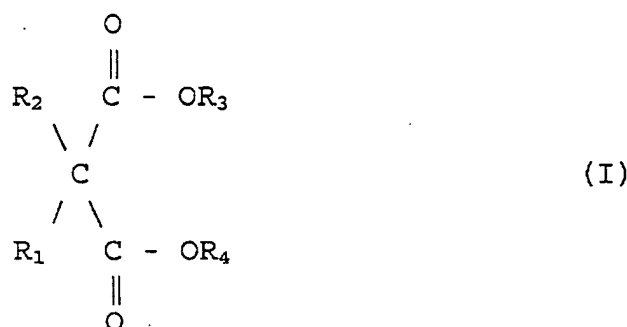
16. Catalyst according to claim 14 or 15 in which the silicon compound is selected from the group consisting of methylcyclohexyldimethoxysilane, diphenyldimethoxysilane, methyl-t-butyldimethoxysilane, dicyclopentyldimethoxysilane, cyclohexyltrimethoxysilane, t-butyltrimethoxysilane and hexyltrimethoxysilane.

17. Process for the (co)polymerization of olefins CH₂=CHR, in which R is hydrogen or a hydrocarbyl radical with 1-12 carbon atoms, carried out in the presence of the catalyst of claim 8.

Patentansprüche

1. Feste Katalysatorkomponente für die Polymerisation von Olefinen CH₂=CHR, worin R Wasserstoff oder einen Kohlenwasserstoffrest mit 1-12 Kohlenstoffatomen darstellt, umfassend eine Titanverbindung mit mindestens einer Ti-Halogenbindung und eine Elektronendonorenbinding, getragen auf einem Mg-Halogenid, wobei die Elek-

tronendonorverbindung ausgewählt ist aus Estern von Malonsäuren der Formel (I) :



worin R_1 eine lineare oder verzweigte $\text{C}_1\text{-C}_{20}$ -Alkyl-, $\text{C}_3\text{-C}_{20}$ -Alkenyl-, $\text{C}_3\text{-C}_{20}$ -Cycloalkyl-, $\text{C}_6\text{-C}_{20}$ -Aryl-, Arylalkyl- oder Alkylarylgruppe darstellt; R_2 eine lineare $\text{C}_1\text{-C}_{20}$ -Alkyl-, lineare $\text{C}_3\text{-C}_{20}$ -Alkenyl-, $\text{C}_6\text{-C}_{20}$ -Aryl-, Arylalkyl- oder Alkylarylgruppe darstellt; R_3 und R_4 unabhängig ausgewählt sind aus der Gruppe, bestehend aus $\text{C}_1\text{-C}_3$ -Alkyl, Cyclopropyl, mit der Maßgabe, dass wenn R_1 lineares oder verzweigtes $\text{C}_1\text{-C}_4$ -Alkyl oder Alkenyl darstellt, R_2 von R_1 verschieden ist.

2. Feste Katalysatorkomponente nach Anspruch 1, wobei R_2 eine lineare $\text{C}_1\text{-C}_{20}$ -Alkyl-, lineare Alkenyl-, Cycloalkyl-, Aryl-, Arylalkyl- oder Alkylarylgruppe darstellt und R_1 $\text{C}_1\text{-C}_4$ -Alkyl, das von R_2 verschieden ist, darstellt.

3. Feste Katalysatorkomponente nach Anspruch 1, wobei mindestens R_1 oder R_2 eine primäre $\text{C}_6\text{-C}_{20}$ -Arylalkylgruppe darstellt.

4. Feste Katalysatorkomponente nach Anspruch 1, wobei die Elektronendonoreverbindung der Formel (I) ausgewählt ist aus der Gruppe, bestehend aus 2,2-Dibenzylmalonsäurediethylester, 2-n-Butyl-2-isobutylmalonsäuredimethylester, n-Bu-tyl-2-isobutylmalonsäurediethylester, 2-Isopropyl-2-n-butylmalonsäurediethylester, 2-Methyl-2-isopropylmalonsäurediethylester, 2-Methyl-2-isobutylmalonsäurediethylester, 2-Isobutyl-2-benzylmalonsäurediethylester.

5. Feste Katalysatorkomponente nach Anspruch 1, wobei das Magnesiumhalogenid MgCl_2 in aktiver Form vorliegt.

6. Feste Katalysatorkomponente nach Anspruch 1, wobei die Titanverbindung TiCl_4 oder TiCl_3 darstellt.

7. Feste Katalysatorkomponente nach Anspruch 1 mit einer Kugelform, einer Oberfläche zwischen 20 und 500 m^2/g und einer Porosität höher als 0,2 cm^3/g .

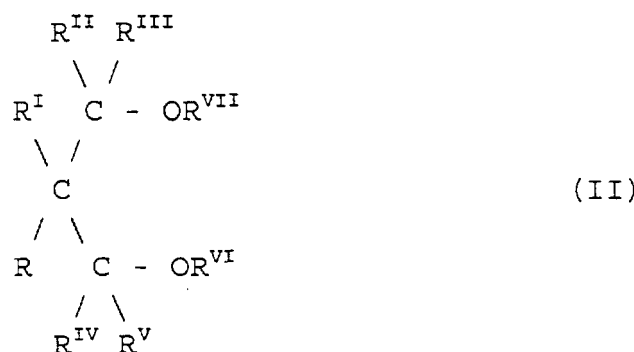
8. Katalysator für die Polymerisation von Olefinen $\text{CH}_2=\text{CHR}$, worin R Wasserstoff oder einen Kohlenwasserstoffrest mit 1-12 Kohlenstoffatomen darstellt, umfassend das Produkt der Reaktion zwischen:

- (i) der festen Katalysatorkomponente von Anspruch 1;
- (ii) einer Alkylaluminiumverbindung und,
- (iii) einer oder mehreren Elektronendonoreverbindungen (äußerer Donor).

9. Katalysator nach Anspruch 8, wobei die Alkylaluminiumverbindung (ii) eine Trialkylaluminiumverbindung darstellt.

10. Katalysator nach Anspruch 9, wobei die Trialkylaluminiumverbindung ausgewählt ist aus der Gruppe, bestehend aus Triethylaluminium, Triisobutylaluminium, Tri-n-butylaluminium, Tri-n-hexylaluminium, Tri-n-octylaluminium.

11. Katalysator nach Anspruch 8, wobei der äußere Donor (iii) ausgewählt ist aus den 1,3-Diethern der allgemeinen Formel (II):



worin R und R^I, R^{II}, R^{III}, R^{IV} und R^V, gleich oder verschieden voneinander, Wasserstoff oder Kohlenwasserstoffreste mit 1 bis 18 Kohlenstoffatomen darstellen und R^{VI} und R^{VII}, gleich oder verschieden voneinander, die gleiche Bedeutung von R-R^V aufweisen, mit der Ausnahme, dass sie nicht Wasserstoff sein können; wobei eine oder mehrere der Gruppen R-R^{VII} zur Bildung eines Cyclus verbunden sein können.

12. Katalysator nach Anspruch 8, wobei der äußere Donor (iii) eine Siliciumverbindung der Formel Ra⁵Rb⁶Si(OR⁷)_c darstellt, worin a und b eine ganze Zahl von 0 bis 2 sind, c eine ganze Zahl von 1 bis 4 ist und die Summe (a+b+c) 4 ist; R⁵, R⁶ und R⁷ Alkyl-, Cycloalkyl- oder Arylreste mit 1-18 Kohlenstoffatomen darstellen.

13. Katalysator nach Anspruch 12, wobei a 1 ist, b 1 ist und c 2 ist.

14. Katalysator nach Anspruch 13, wobei R₅ und/oder R₆ verzweigte Alkyl-, Cycloalkyl- oder Arylgruppen mit 3-10 Kohlenstoffatomen sind und R₇ eine C₁-C₁₀-Alkylgruppe, insbesondere Methyl, darstellt.

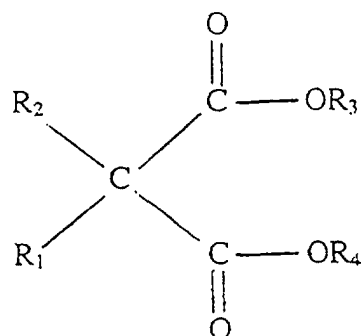
15. Katalysator nach Anspruch 12, wobei a 0 ist, c 3 ist und R⁶ eine verzweigte Alkyl- oder Cycloalkylgruppe darstellt und R⁷ Methyl darstellt.

16. Katalysator nach Anspruch 14 oder 15, wobei die Siliciumverbindung ausgewählt ist aus der Gruppe, bestehend aus Methylcyclohexyldimethoxysilan, Diphenyldimethoxysilan, Methyl-t-butyltrimethoxysilan, Dicyclopentyltrimethoxysilan, Cyclohexyltrimethoxysilan, t-Butyltrimethoxysilan und t-Hexyltrimethoxysilan.

17. Verfahren für die (Co)polymerisation von Olefinen CH₂=CHR, worin R Wasserstoff oder einen Kohlenwasserstoffrest mit 1-12 Kohlenstoffatomen darstellt, ausgeführt in Gegenwart des Katalysators nach Anspruch 8.

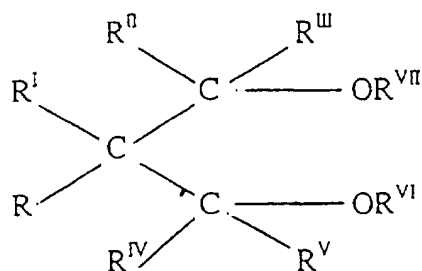
Revendications

1. Un composant de catalyseur solide pour la polymérisation d'oléfines CH₂=CHR où R est l'hydrogène ou un radical hydrocarbyle comportant 1 à 12 atomes de carbone, comprenant un dérivé de titane, présentant au moins une liaison Ti-halogène, et un composé donneur d'électron supporté sur un halogénure de magnésium, dans lequel ledit composé donneur d'électron est choisi parmi les esters des acides maloniques de formule (I):



dans laquelle R_1 est un groupe alkyle, linéaire ou ramifié, en C_1 à C_{20} , alkényle en C_3 à C_{20} , cycloalkyle en C_3 à C_{20} , en un groupe C_6 à C_{20} , aryle, arylalkyle ou alkylaryle ; R_2 est un groupe alkyle linéaire en C_1 à C_{20} , alkényle linéaire en C_3 à C_{20} , aryle arylalkyle ou alkylaryle en C_6 à C_{20} ; R_3 et R_4 sont indépendamment choisis dans le groupe consistant en alkyle en C_1 à C_{20} , cyclopropyle, avec cette condition que si R_1 est un alkyle ou un alkényle linéaire ou ramifié en en C_1 à C_4 , R_2 est différent de R_1 .

2. Un composant de catalyseur solide selon la revendication 1, dans lequel R_2 est un groupe en C_1 à C_{20} , alkyle linéaire, alkényle linéaire, cycloalkyle, aryle, arylalkyle ou alkylaryle, et R_1 est un alkyle en C_1 à C_4 , différent de R_2 .
3. Un composant de catalyseur solide selon la revendication 1, dans lequel au moins R_1 ou R_2 est un groupe arylalkyle primaire en C_6 à C_{20} .
4. Un composant de catalyseur solide selon la revendication 1, dans lequel le composé donneur d'électron de formule (I) est choisi dans le groupe consistant en diéthyl-2,2-dibenzylmalonate, diméthyl-2-n-butyl-2-isobutylmalonate, diéthyl-n-butyl-2-isobutylmalonate, diéthyl-2-isopropyl-2-n-butylmalonate, diéthyl-2-méthyl-2-isopropylmalonate, diéthyl-2-méthyl-2-isobutylmalonate, diéthyl-2-isobutyl-2-benzylmalonate.
5. Un composant de catalyseur solide selon la revendication 1, dans lequel l'halogénure de magnésium est MgCl_2 sous forme active.
6. Un composant de catalyseur solide selon la revendication 1, dans lequel le dérivé de titane est TiCl_4 ou TiCl_3 .
7. Un composant de catalyseur solide selon la revendication 1 ayant une forme sphérique, une surface spécifique comprise entre 20 et 500 m^2/g et une porosité supérieure à 0,2 cm^3/g .
8. Un catalyseur de la polymérisation d'oléfines $\text{CH}_2=\text{CHR}$, où R est l'hydrogène ou un radical hydrocarbyle comportant 1 à 12 atomes de carbone, comprenant le produit de la réaction entre :
 - (i) le composant de catalyseur solide de la revendication 1 ;
 - (ii) un dérivé alkylaluminium ; et
 - (iii) un ou plusieurs composés donneurs d'électrons (donneur externe).
9. Un catalyseur selon la revendication 1, dans lequel le dérivé alkylaluminium (ii) est un dérivé trialkylaluminium.
10. Un catalyseur selon la revendication 9, dans lequel le dérivé trialkylaluminium est choisi dans le groupe consistant en triéthylaluminium, triisobutylaluminium, tri-n-butylaluminium, tri-n-hexylaluminium, tri-n-octylaluminium.
11. Un catalyseur selon la revendication 1, dans lequel le donneur externe (iii) est choisi parmi les 1,3-diéthers de formule générale (II):



dans laquelle R et R^I, R^{II}, R^{III}, R^{IV} et R^V, identiques ou différents les uns des autres, sont l'hydrogène ou des radicaux hydrocarbonés comportant 1 à 18 atomes de carbone, et R^{VI} et R^{VII}, identiques ou différents les uns des autres, ont la même signification que R-R^I, sauf qu'ils ne peuvent pas être de l'hydrogène ; un ou plusieurs des R-R^{VII} peuvent être reliés pour former un cycle.

12. Un catalyseur selon la revendication 8, dans lequel le donneur externe (iii) est un dérivé du silicium de formule R_a⁵R_b⁶Si(OR⁷)_c, où a et b sont des entiers de 0 à 2, c est un entier de 1 à 4 et la somme (a+b+c) vaut 4 ; R⁵, R⁶ et R⁷ sont des radicaux alkyle, cycloalkyle ou aryle comportant 1 à 18 atomes de carbone.

13. Un catalyseur selon la revendication 12, dans lequel a vaut 1, b vaut 1 et c vaut 2.

14. Un catalyseur selon la revendication 13, dans lequel R₅ et/ou R₆ sont des groupes alkyle, cycloalkyle ou aryle ramifiés à 3 à 10 atomes de carbone et R₇ est un groupe alkyle en C₁ à C₁₀, en particulier méthyle.

15. Un catalyseur selon la revendication 12, dans lequel a vaut 0, c vaut 3 et R⁶ est un groupe alkyle ramifié ou cycloalkyle et R⁷ est un groupe méthyle.

16. Un catalyseur selon l'une quelconque des revendications 14 ou 15, dans lequel le dérivé de silicium est choisi dans le groupe consistant en méthylcyclohexyldiméthoxysilane, diphényldiméthoxysilane, méthyl-t-butyl-diméthoxysilane, dicyclopentyldiméthoxysilane, cyclohexyltriméthoxysilane, t-butyltriméthoxysilane et t-hexyltriméthoxysilane.

17. Un procédé de (co)polymérisation d'oléfines CH₂=CHR dans lequel R est l'hydrogène ou un radical hydrocarbyle comportant 1 à 12 atomes de carbone, effectué en présence du catalyseur selon la revendication 8.